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(54) Superpurifier for nitrogen and process for purifying same

(57) A superpurifier for nitrogen provides means for contacting an impurity-containing nitrogen gas with a getter of an alloy consisting of from 15 to 30% by weight iron and from 70 to 85% by weight zirconium. A higher purity than that obtained by conventional purification processes is given.

Fig. 1

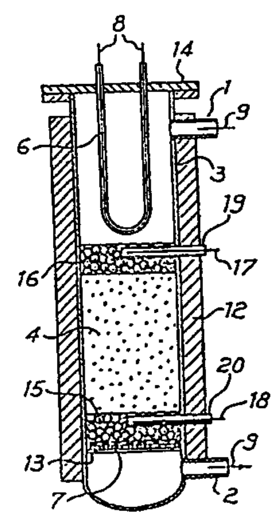

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Fig. 3

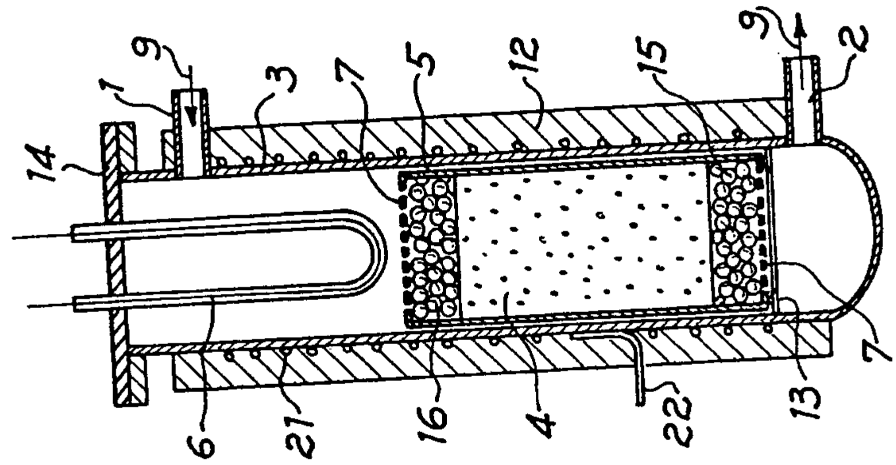


Fig. 2

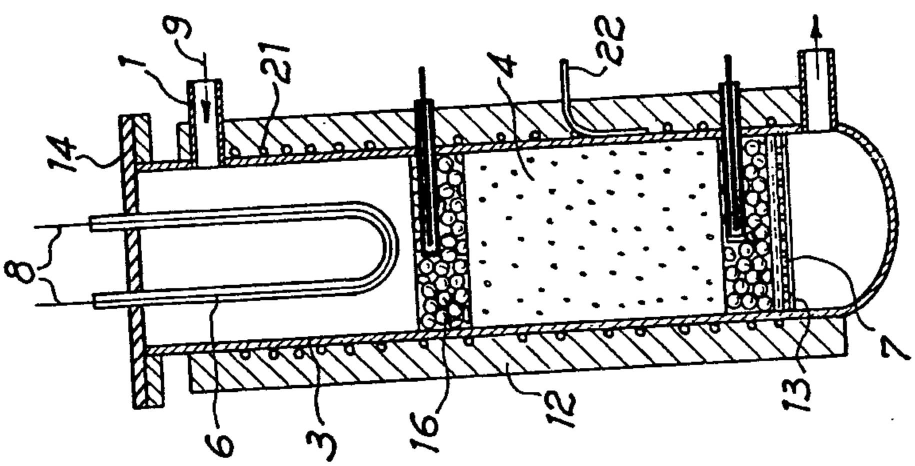
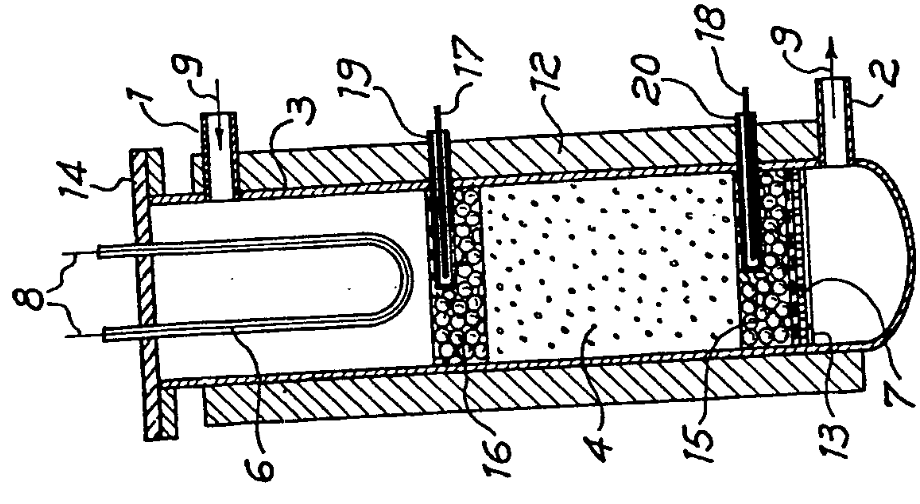


Fig. 1



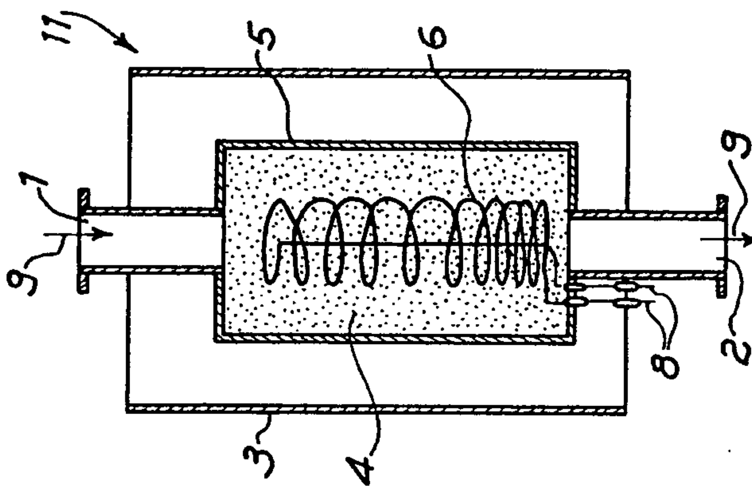


Fig.6

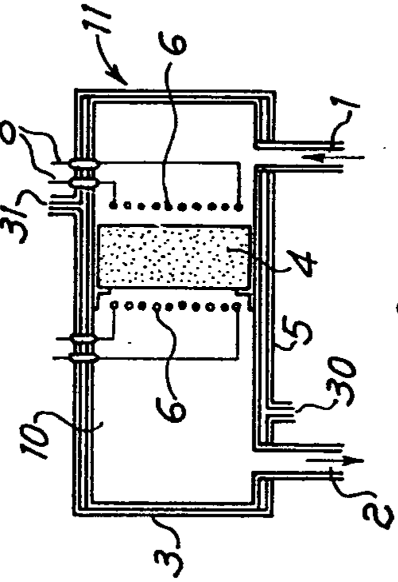


Fig.5

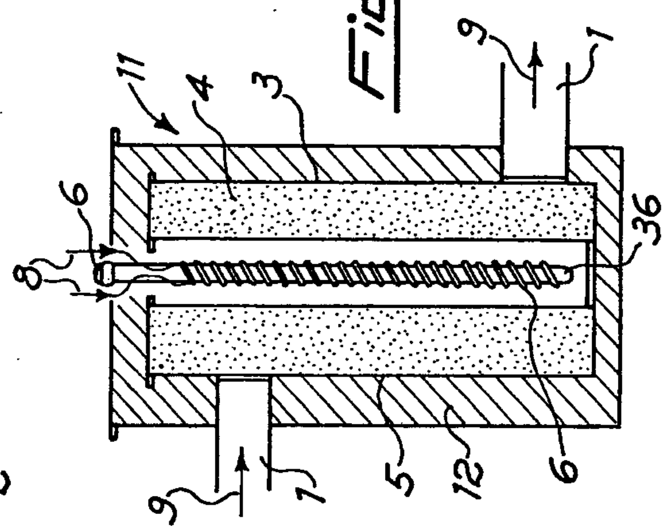


Fig.7

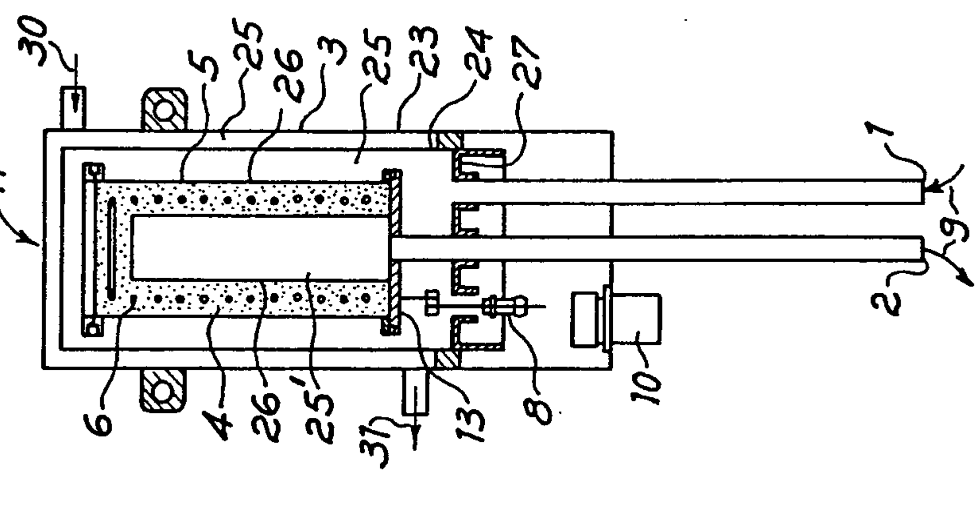
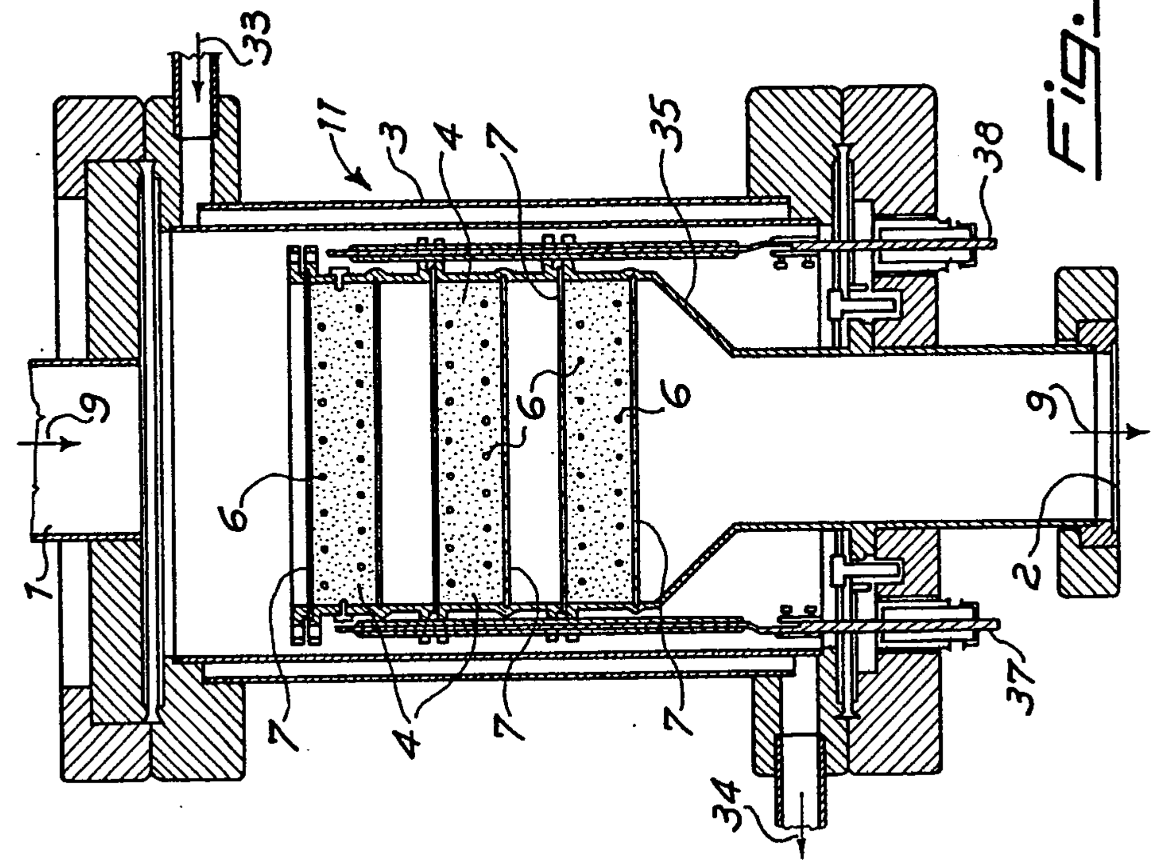


Fig.4


1
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33
11
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37
34

Fig.9

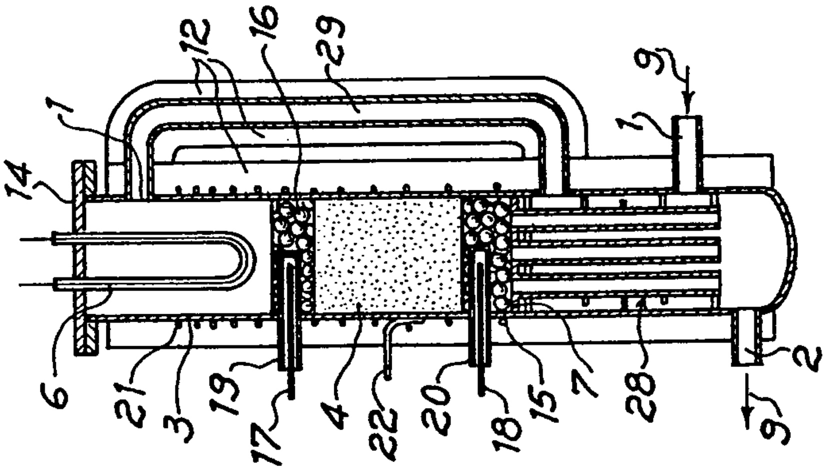
12
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Fig.8

SPECIFICATION

Superpurifier for nitrogen and process for purifying same

Nitrogen is a useful gas enjoying steadily growing demand in many sectors of industry including the fields of electronics, chemicals, iron and steel making, and shipbuilding.

It has been a common industrial process for the production of nitrogen to repeat compression of air by a compressor and adiabatic expansion of the compressed air until liquid air is obtained and then subject it to fractional distillation under high pressure to produce liquid nitrogen of high purity. The product is filled either in liquid or gaseous form into cylinders and put on the market.

A typical inert gas, nitrogen is widely used in the aforementioned fields to provide atmospheres for heat treatments of metals, for the manufacture of semiconductors and the like. When it is to be employed in superfine microprocessing such as in electronics industry, it must be further purified by removing impurities to a higher purity immediately before use. For large-volume consumption in industrial operations it is customary to vaporize liquid nitrogen and supply the resulting gas through pipelines. Here the problem is how to meet the requirement of rapid and positive removal of the impurities, such as oxygen, hydrogen, carbon monoxide, carbon dioxide, hydrogen, hydrocarbons, and water, from the gasified nitrogen.

In order to remove these impurities and purify nitrogen to high purity, various nitrogen gas purifiers have heretofore been marketed and used. For instance, one of the applicants, Taiyo Sanso Co., has since 1974 sold gas purifiers (Models TIP-10, -30, -60, -100, -200, -300, -400, and -500). These and other commercially available gas purifiers use oxidation catalysts of metal oxides such as of nickel, chromium, and copper to oxidize carbon monoxide, hydrocarbons, hydrogen and the like into carbon dioxide and water and then remove impurities by adsorption from the resultants by the use of a zeolite molecular sieve, active charcoal or the like for the gas purification. Where high-purity nitrogen is to be simply obtained, these gas purifiers are convenient and are therefore in wide use.

The impurities in the gas purified by these existing equipment, according to the manufacture's brochures, are generally as follows:

Constituent	*Oxygen*	*Hydrocarbon*	*Carbon dioxide*	*Moisture*
ppm	<0.1	<0.1	<0.4	<0.5 (dew point −80°C)

To this end, the use of hydrogen-occluding alloys, namely, Ti-Mn, Ti-Fe, and rare-earth-Ni alloys, have been proposed in Japanese Patent Application Public Disclosure No. 156308/1982. They have, however, failed to purify nitrogen beyond the level tabulated above.

The commercially available gas purifiers as mentioned above are simple, convenient, and efficient for obtaining high-purity nitrogen gas. However, the recent progress of the semiconductor industry suggests that more and more precise microprocessing and hence nitrogen gas of even higher purity will be required for future production of highly integrated circuits. In fact, there is already strong demand for high-purity gas for testing purposes. The technical problem the present invention is intended to solve is lowering the current levels of impurities according to the prior art technology to much lower levels, by one Figure in parts per million.

We have intensively studied on the means for purifying nitrogen gas to decrease its impurity concentrations by one order of magnitude in ppm each from the usual levels as stated above. As a result, we have arrived at an apparatus and a process capable of purifying the conventionally purified gas of high purity to an even higher purity. The present invention has now been perfected on this basis.

The apparatus according to this invention is a superpurifier for nitrogen comprising an outer shell provided with an inlet for nitrogen gas to be purified, an outlet for purified nitrogen gas, a gas flow passage connecting the gas inlet and outlet, at least one getter chamber packed with a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and disposed midway in the gas flow passage, and heater means to maintain the getter at the temperature at which it functions.

The process according to the invention is based on a process for purifying nitrogen characterized by the steps of first conventionally purifying impure nitrogen gas by passing it through a bed of metal oxide catalyst for oxidation at an oxidation reaction temperature and then through an adsorbent bed of zeolite molecular sieve or the like, and thereafter removing the remaining impurities by adsorption from the nitrogen gas of low impurity contents by further passing it through a getter bed packed with a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and maintained at a temperature of 20° to 500°C.

As the getter for use in the invention which is an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium, the one described in U.S. Patent Specification No. 4,306,887 may be employed.

In view of the characteristic of the getter of iron-zirconium alloy that does not adsorb nitrogen but adsorbs other impurities selectively, particularly desirable is a getter of an alloy consisting of from 22 to 25% by weight of iron and from 75 to 78% by weight of zirconium.

The getter of such an iron-zirconium alloy is substantially a non-adsorbent for nitrogen but practically completely adsorbs and removes impurities such as carbon dioxide, moisture, and hydrogen at a temperature

between 20° and 500°C.

The iron-zirconium composition is desired to range from 15 to 30% by weight of iron and 85 to 70% by weight of zirconium. At higher percentage zirconium contents the alloy starts to sorb significant amounts of nitrogen, the gas which is required to be purified and not sorbed, whereas at lower percentage zirconium contents the efficiency of removal (sorption) of active gases from the nitrogen is considerably reduced.

It is desirable that the getter alloy be used in the form of an intermetallic compound, which is readily pulverized and can be handled with ease. Moreover, the increased surface area renders the powdered material more active.

The process for the preparation of such an alloy may generally conform to the procedure described in U.S. Patent Specification No. 4,312,669 that teaches the manufacture of a ternary iron-zirconium-vanadium ally. Following practically the same procedure but omitting the addition of vanadium, a desired alloy can be made. Commercially available products, made and sold by SAES Getters S.p.A. of Milan, Italy, are appropriate for this use.

The binary alloy getter is packed in at least one bed zone provided in a gas flow passage connecting an inlet for impure nitrogen gas and an outlet for purified nitrogen gas of an outer shell. The getter bed combines with a heater means associated with the outer shell for maintaining the getter at its adsorption reaction temperature to constitute the essential parts of the nitrogen superpurifier according to the invention. Nitrogen to be purified is passed through this superpurifier so that its impure contents are brought into contact with the getter and are removed by adsorption.

The getter to be packed in the chamber takes the form of pellets in preference to fine particles since the former are easier to provide sufficient interstices therebetween for the gas flow. Also, the getter as pellets of uniform size rather than small lumps irregular in size renders it easy to maintain a constant void ratio in the getter bed, to design the apparatus, and to reproduce the good performance. Thus, while the getter in the form of fine particles or small lumps is not objectionable, the use of pelletized getter, compression molded of the alloy powder, is preferred as it better meets the requirements for industrial designing and manufacture of the nitrogen gas superpurifier.

The heater means to be incorporated in the apparatus of the invention to keep the getter hot enough for the adsorption reaction may take varied forms as will be explained later in connection with preferred embodiments of the invention. The heating method may be electric heating or indirect heating by the use of a heating medium circulated through a double-wall structure or the like. Also, the heating zone may be suitably chosen, for example, in the gas preheating region upstream of the getter bed or chamber, or around or inside the getter mass. Since it is desirable that sufficient heating be done to effect a smooth adsorption reaction of the getter with the gas and produce as uniform a temperature distribution as feasible, the combination of the heating method and zone may be varied, according to the necessity, to best attain the end.

While it is possible that the getter chamber in the apparatus of the invention be provided inside the outer shell, as directly packed in the latter, a preferred arrangement is such that the getter bed consists of at least one cartridge packed with the getter material and which is adapted to be fitted in the outer shell detachably for ease of replacement. The getter components according to this invention adsorb and remove impurities from impure nitrogen by chemical adsorption that involves chemical changes. They therefore are consumed stoichiometrically and have a limited life. After service for a predetermined period the getter must be replaced by fresh one; otherwise the purpose of superpurifying nitrogen will no longer be achieved. To this end the superpurifier including the outer shell packed with the getter may be handled as a single unit and replaced as such from time to time. It is also possible to fill up the getter in a cartridge instead and dismount the cartridge from the outer shell for replacement at proper intervals of time.

The cartridge desirably employs a metal case so perforated as to facilitate the gas flow.

Because the superpurifier of the invention is intended to purify nitrogen until the concentrations of its ingredients as impurities are reduced to about 0.01 ppm or less each, it is advisable that the inner wall portion of the apparatus with which nitrogen gas comes in contact be made of a metal polished on the surface to be close-grained and smooth enough to minimize gas adsorption and which does not form powder due to corrosion. Such metals include, for example, but are not limited to, stainless steels, Hastelloy, Incoloy, and Monel metal. Any other metal material which satisfies the above requirements may be suitably chosen and used.

As stated above, the inner wall material of the apparatus that contacts the nitrogen gas is desired to have a densely and smoothly polished surface to minimize gas adsorption. The desirable degree of smoothness of the polished surface is numerically defined to be such that the roughness of the inner wall surface to contact nitrogen gas is 0.5 μm or less, preferably 0.25 μm or less in terms of the centerline average height (R_a) [Japanese Industrial Standard (JIS) B 0601-1970]. This numerical range is not always critical but is recommended as a dependable, safe range.

Although the polished inner wall material is advantageously used in the zone where the gas flowing out of the cartridge chamber comes in contact, it is, of course, possible to use it also in the zone where the gas passing through the cartridge contacts. In many cases it is rather inconvenient to use the polished material only in the zone where the gas that has flowed past the cartridge contacts. The surface polishing and baking will markedly shorten the time period required before highly-purified gas begins to be obtained at a constant rate, even from a new apparatus.

In the apparatus of the present invention the means for solving the technical problem before it can be

variously embodied as suggested above. Thus it is to be understood that the invention is not limited to the specific embodiments thereof so far described but various modifications may be made without departing from the spirit and scope of the invention.

In the process of the invention it is essential that the nitrogen gas to be purified be passed through the bed of a metal-oxide oxidation catalyst as its oxidation reaction temperature. This is because the lack of adsorbability of the getter used in the invention with respect to methane and other hydrocarbons which must therefore be removed by converting the hydrocarbons and carbon monoxide contained in the nitrogen gas into water and carbon dioxide and removing most of them by adsorption by passage through an adsorbent bed of zeolite molecular sieve or the like.

The nitrogen gas purified to low impurity contents by, e.g., the known purification process is passed through a getter bed packed with a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and maintained at a temperature in the range of 20° to 500°C, so that the impurities contained in the nitrogen are adsorbed away. If the reaction temperature at which the impurities are removed by adsorption from the nitrogen gas in the getter bed is below 20°C, the impurities are adsorbed by the getter surface but cannot be expected to diffuse into the getter mass. Thus the adsorption practically comes to an end in the state of saturation on the surface, without fully making use of the getter capacity. In the specified range of 20° to 500°C the getter performs adsorption to the full, allowing the impurities to diffuse thoroughly therein. The apparent life of the getter is accordingly extended.

On the other hand, in the temperature region above 500°C, nitrogen gas is easily adsorbed by the getter. Setting a reaction temperature in excess of 500°C is therefore undesirable.

Within the specified temperature range of 20° to 500°C, a narrower range of 350° to 450°C is most preferred. A temperature in the latter range is the most recommendable reaction temperature in that it assures a high adsorption rate and thorough diffusion of the impurities into the bed of getter with no possibility of hydrogen desorption.

The present invention will now be described in more detail below, by way of example only, in connection with embodiments thereof.

Nitrogen superpurifiers embodying the invention are illustrated in Figures 1 through 9. Figure 1 shows a nitrogen superpurifier comprising: an outer shell 3 made of a stainless steel tube (grade SUS 304 TP conforming to Japanese Industrial Standard JIS C 3448) which has a nitrogen inlet 1 formed near the top and a nitrogen outlet 2 near the bottom, the shell being covered with a heat insulator 12 all over the surface; a top cover 14 fitted to the top of the outer shell 3; a heater 6 inserted through the top cover 14 into the space 25 inside the shell; a bed of getter 4 packed in the space defined below the heater 6 between upper and lower buffers 16, 15; and a perforated plate 7 held by a support 13 which in turn is secured to the inner wall of the outer shell and is supporting the bed as well as the perforated plate. The getter used was an iron (22-25 wt%)-zirconium (75-78%) alloy getter manufactured and marketed by SAES Getters S.p.A., in the form of columnar pellets having a diameter of 3 mm and height of 4 mm.

The buffers, indicated at 15, 16, consist of a layer each of small alumina spheres 4 mm in diameter packed up to a height of about 5 cm. They correct any uniform flow of the gas through the getter bed, keep the fine particles of the getter from scattering, and uniformalize the temperature distribution.

While the embodiment being described uses small alumina spheres in forming the buffers, small stainless steel balls or a stack of fine-mesh stainless steel screens may be employed instead. Also, the buffers are not always used, and a buffer-less embodiment will be described later.

In the upper portions of the buffers 15, 16 are embedded sheathes 20, 19 accommodating thermometers 18, 17, respectively.Chromel-Alumel thermocouples are used as the thermometers.

Nitrogen gas 9 to be purified is introduced into the vessel at the inlet 1, heated by the heater 6, passes through the upper buffer 16 and thence, as a uniform flow, through the bed of getter 4 where it is freed from impure gas contents by adsorption. The purified gas is led through the perforated plate 7 and taken out of the vessel at the outlet 2.

Figure 2 and following figures show other embodiments of the invention. Throughout these figures like parts are designated by like numerals and the description is omitted or minimized each.

Figure 2 shows a superpurifier of the same construction as the embodiment in Figure 1 expecting that an electric heater 21 is coiled round the outer shell 3 and a thermocouple 22 is installed to measure the heater temperature. This modification facilitates the temperature control of the getter bed.

Although Figures 1 and 2 illustrate the embodiments in which the bed of getter 4 is directly packed in the outer shell 3, the getter bed may be separately provided as well. Figure 3 shows an arrangement of cartridge 5 where the getter 4 and buffers 15, 16 are accommodated in a cylinder equipped with perforated plates 7 at both ends. After service for a given period, the cartridge 5 may be taken out by removing the top cover 14 and replaced by a new one. This permits more efficient operation than with the arrangements of Figures 1 and 2.

Figure 4 shows another embodiment 11, in which the outer shell 3 is of a double-wall construction, consisting of an inner wall 24 and an outer wall 23. The space between the walls provides a passage through which a heating medium such as steam flows from a heating medium inlet 30 to an outlet 31. In the space defined by the inner wall is accommodated a cartridge 5 containing a getter 4, with a coil of electric heater 6 embedded in the getter. The heater 6 is connected to an external power source not shown through leads 8 (only one of them being shown) and a terminal assembly 10. The cartridge 5 has inner and outer porous walls 26 concentrically held in spaced relation by a support 13. The inner wall 24 of the outer shell is abutted at its

lower end against a bottom plate with a flange 27, through which a gas inlet pipe 1 and an outlet pipe 2 extend. The pipe 2 serves also to support the cartridge 5. Nitrogen gas 9 to be purified is fed through the inlet 1 into the outer space 25, heated there to a proper temperature, and thence forced through the porous wall 26 into the getter layer 4 for purification. The purified gas flows out into the inner space 25' and is taken out via the outlet 2.

Figure 5 shows still another embodiment of superpurifier 11. The outer shell 3 is again of double-wall construction, with a space formed therein to circulate a heating medium introduced at an inlet 30 and discharged at an outlet 31 to perform temperature control. Inside the inner wall is disposed a cartridge 5 packed with a getter 4 between porous walls. On both sides of the cartridge are arranged heaters 6 which are connected to external power sources through leads 8. Impure nitrogen gas 9 is fed at an inlet 1, preheated by the heating medium, purified by passage through the getter mass 4 kept at a given temperature by the heaters 6, and then taken out at an outlet 2.

Yet another embodiment of superpurifier 11 is shown in Figure 6. A cylindrical outer shell 3 supports a cartridge 5 by means of upper and lower plates (not shown). The cartridge 5 comprises a built-in electric heater 6 with leads 8 and a mass of getter 4 filled in the space between upper and lower perforated plates or buffer layers, with the heater embedded therein.

Figure 7 shows another apparatus 11 embodying the invention. An inner cylinder is provided inside an outer shell 3 which consists of inner and outer walls and a heat insulator 12 filling up the space between the walls. A getter 4 is packed in the space between the inner cylinder and the outer shell, and an electric heater 6 coiled round a ceramic rod 36 is inserted into the central space in the inner cylinder. Nitrogen gas 9 to be purified enters the vessel at an inlet 1, passes through the getter 4, and the purified gas leaves the vessel at an outlet 2.

Figure 8 shows another embodiment, which is a modification of the superpurifier illustrated in Figure 3 and is characterized by means for recovering the heat of purified nitrogen. Nitrogen 9 to be purified enters a heat exchanger 28 installed under the purifier body, undergoes heat exchange with the outgoing gas, and the gas so preheated moves through a pipe 29 surrounded by a heat insulator 12 and through an upper inlet 1 into a bed of getter 4. The purified gas is cooled in the heat exchanger and leaves the purifier at an outlet 2.

Figure 9 shows a further embodiment. The outer shell 3 is a double-wall cylinder, and a heating medium is introduced into the space between the walls at an inlet 33 and is discharged at an outlet 34. Inside the outer shell 3 is disposed a gas-tight cartridge 35. The space in the cartridge case is partitioned horizontally with a plurality of perforated plates 7, and a plurality of getter beds 4 are formed, each filling up the space formed by every other pair of the perforated plates. The getter beds have electric heaters 6 embedded therein, one for each, and supplied with electricity through leads 37, 38. Nitrogen gas 9 to be purified flows in at an inlet 1 and the purified gas flows out at an outlet 2.

Examples of the invention which used a specific getter composition will now be explained.

The instruments used for gas analyses in the examples were as follows:

Gas analysis instrument:
Gas chromatograph-mass spectrometer, Model TE-360B
(mfd. by Anelva Corp.)
Gas chromatograph-F.I.D., Model GC-9A
(mfd. by Shimadzu Seisakusho, Ltd.)

Moisture meter:
Hygrometer, Model 700
(mfd. by Panametric Co.)

Surface roughness meter:
Surfcorder, Model SE-3H
(mfd. by Kosaka Laboratory Co., Ltd.)

Example 1

A powdered non-evaporable getter alloy having a weight composition of 76.6% zirconium and 23.4% iron and a particle size of between 50 and 250 μm were placed in the superpurifier for nitrogen shown in Figure 1. The stainless steel (trade designation, SUS 304) cylinder had an outside diameter of 21.7 mm and an inside diameter of 17.5 mm, its length being 350 mm. The length of cylinder occupied by the getter material was 200 mm, and the heights of the upper and lower buffers of alumina spheres were 5 cm each. Impure nitrogen gas was introduced into the superpurifier at a temperature of 25°C and a pressure of 6 kg/cm^2 (gauge) at a flow rate of 0.17 l/min. The nitrogen flowed through the getter bed held at 375°C and issued at a pressure of 4 kg/cm^2 (gauge) from the outlet. Its impurity level was measured for various gases 40 minutes after the start of the flow of the gas. The results of Table I were obtained.

TABLE I

Impurity	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	0.4	0.006
CH_4	0.01	0.01
CO	0.06	0.008
CO_2	0.04	0.007
H_2O	3.0	no trace

The level of impurities in the outlet gas remained constant for 1030 hours.

Example 2

Pellets were produced having a diameter of 3 mm and height of 4 mm by compressing and pelletizing a non-evaporable getter alloy having a composition and particle size identical to those of the getter alloy of Example 1. The pellets were loaded into the superpurifier shown in Figure 2. The stainless steel (SUS 304) cylinder had an outer diameter of 89.1 mm and an inner diameter of 83.1 mm. Its length was 660 mm. The length of the cylinder occupied by the pellets of getter material, including the thickness of the upper and lower buffers (of alumina spheres) each having a bed height of 5 cm, was 185 mm. Impure nitrogen was introduced into the superpurifier at a temperature of 25°C and a pressure of 4 kg/cm^2 (gauge) at a flow rate of 12 l/min.

The impure nitrogen flowed through the non-evaporable getter bed held at a temperature of 375°C by means of a spiral resistance heater and issued at a pressure of 3.95 kg/cm^2 (gauge) from the outlet. Its impurity level was measured for various gases 40 minutes after the start of the flow of nitrogen. The results obtained were as shown in Table II.

TABLE II

Impurity	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	11.29	0.006
CH_4	0.01	0.01
CO	8.8	0.008
CO_2	8.3	0.007
H_2O	5.0	no trace

The level of the impurities in the outlet gas remained constant for 760 hours.

Example 3

Pellets were produced exactly as in Example 2 and placed in the cartridge shown in Figure 3. The cartridge had an outside diameter of 80 mm, an inside diameter of 78 mm, and length of 244 mm. The same mass of pellets was used as in Example 2. The cartridge was then placed in a cylinder identical to that of Example 2 (except that its length was 719 mm). Impure nitrogen was caused to flow through the superpurifier at the same inlet pressure, temperature, and flow rate as described in Example 2. The cartridge was maintained at 375°C. The outlet gas pressure and composition were found to be identical to those found in Example 2 at the point 40 minutes after the start of the flow of nitrogen. The level of the impurities in the outlet gas again remained constant for 760 hours.

Example 4

In this example the procedure of Example 2 was followed in all respects except that the inner surface roughness of the cylinder was $R_a = 0.5\ \mu m$ (normally $R_a = 2.5\ \mu m$) and the stainless steel outlet piping had an outside diameter 9.5 mm, inside diameter 7.5 mm, and an inner surface roughness of $R_a = 0.2\ \mu m$. The results shown in Table III were obtained 40 minutes after the start of the flow of nitrogen.

TABLE III

Impurity	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	11.29	0.003
CH_4	0.01	0.01
CO	8.8	0.008
CO_2	8.3	0.003
H_2O	5.0	no trace

The level of the impurities in the outlet gas remained constant for 760 hours.

Example 5

In this example nitrogen gas to be purified was first passed through a stainless steel (SUS 304) cylinder having an outside diameter of 89.1 mm, inside diameter of 83.1 mm, and length of 660 mm filled to a bed height of 185 mm with pellets (3 mm in diameter and 4 mm in length) and maintained at a temperature of 450°C. The pellets are advantageously pellets of copper oxide. Then, the water vapor content of the nitrogen gas to be purified was reduced by passing it through a dryer consisting of a stainless steel (SUS 304) cylinder having an outside diameter of 89.1 mm, inside diameter of 83.1 mm, and length of 660 mm filled to a bed height of 200 mm with a molecular sieve type 5-A, the pellet size being 3.2 mm across and 24 mm long. This gas was treated by the procedure of Example 2. The outlet pressure from the dryer bed and therefore the inlet pressure to the superpurifier was 4 kg/cm^2 (gauge). The temperature was varied to see the effects of different getter temperatures. The results are given in Table IV.

TABLE IV

Inlet impurity level (ppm)		*Outlet impurity level (ppm) at temperature* 20°C	250°C	375°C	500°C
O_2	11.29	0.006	0.006	0.006	0.004
CH_4	3.7	0.009	0.009	0.009	0.009
CO	8.8	0.008	0.008	0.008	0.004
CO_2	8.3	0.007	0.007	0.007	0.004
H_2O	5.0	no trace	no trace	no trace	no trace
Outlet gas remained constant for		21 hr	1050 hr	2330 hr	2390 hr
Power consumption of getter cyl.		0	0.61 kW/h	1.1 kW/h	1.7 kW/h

The table indicates that the getter of the invention exhibits excellent purification capability in the temperature range of 20° to 500°C.

Examples 6 and 7

Pellets were produced having a diameter of 3 mm and a length of 4 mm by compression of non-evaporable getter powders consisting of an alloy of Zr 84% and Fe 16% by weight (Example 6) and an alloy of Zr 71% and Fe 29% by weight (Example 7) and having particle sizes of 50 - 250 μm (150 μm in average). These pellets were loaded into a superpurifier having the same construction in the same manner as Example 2. Nitrogen gas containing impurities was introduced into the superpurifier at a temperature of 25°C, pressure of 4 kg/cm^2 (gauge) and a flow rate of 12 l/min.

The impurity-consisting nitrogen gas was passed through the bed of the non-evaporable getter kept at a temperature of 375°C by means of a spiral resistance heater and emerged from the outlet at a pressure of 3.95 kg/cm^2 (gauge). The impurity level was measured 40 min after the start of the flow of the nitrogen gas and the results in Table V were obtained.

TABLE V

Gas	*Inlet impurity (ppm)*	*Outlet impurity Ex 6 (ppm)*	*Ex. 7 (ppm)*
O_2	11.29	0.003	0.01
CH_4	0.01	0.01	0.01
CO	8.8	0.005	0.009
CO_2	8.3	0.005	0.01
H_2O	5.0	no trace	no trace

The outlet impurity levels were constant for 960 hrs and 690 hrs, respectively.

CLAIMS

1. A superpurifier for nitrogen comprising an outer shell provided with an inlet for nitrogen gas to be purified, an outlet for purified nitrogen gas, a gas flow passage connecting the gas inlet and outlet, at least one getter chamber containing

a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and disposed

in the gas flow passage, and heater means to maintain the getter at the temperature at which it functions.

2. A superpurifier as defined in claim 1 characterized in that said getter alloy to be used in said getter chamber is in the form of pellets made by compressing and pelletizing a powdered iron-zirconium alloy.

3. A superpurifier as defined in claim 1 characterized in that said alloy for use as the getter has a composition of from 22 to 25% by weight of iron and from 75 to 78% by weight of zirconium.

4. A superpurifier as defined in claim 1 characterized in that said alloy for use as the getter is an intermetallic compound of iron and zirconium.

5. A superpurifier as defined in claim 1 characterized in that said getter chamber comprises at least one cartridge packed with said getter, and that said cartridge is detachably installed in said outer shell so that it can be easily replaced by new one.

6. A superpurifier as defined in claim 5 characterized in that each said cartridge comprises a perforated metal container packed with said getter.

7. A superpurifier as defined in claim 1 characterized in that the apparatus material with which the nitrogen gas comes in contact is such that the inner wall surface to contact the gas has been polished to a surface roughness (R_a) of 0.5 μm or less in terms of the centerline average height given by the average amplitude over the entire measurement section.

8. A superpurifier as defined in claim 1 characterized in that a pretreatment unit for removing hydrocarbons is added thereto.

9. A superpurifier as defined in claim 8 characterized in that said pretreatment unit to be used for removing hydrocarbons comprises an oxidizer means provided with a bed of a metal oxide catalyst for oxidation through which nitrogen gas is to pass and an adsorber means provided with an adsorbent bed of zeolite molecular sieve or the like through which the nitrogen gas containing water, carbon monoxide, carbon dioxide, and other impurities produced by the oxidation reaction is to pass.

10. A process for superpurifying nitrogen characterized by the steps of purifying nitrogen gas to be purified by the usual gas purification process of passing impure nitrogen gas through a bed of a metal oxide catalyst for oxidation at an oxidation reaction temperature and then passing the gas through an adsorbent bed of zeolite molecular sieve or the like, and thereafter removing the remaining impurities by adsorption from the nitrogen gas of low impurity level by passing it further through a getter bed packed with a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and maintained at a temperature of 20° to 500°C.

11. A process as defined in claim 10 characterized by the use of a getter bed packed with a getter of an alloy consisting of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium and maintained at a temperature of 350° to 450°C.

12. A process for purifying nitrogen which comprises passing the nitrogen through a getter bed comprising a getter of an alloy of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium at a temperature of 20° to 500°C.

13. A process for superpurifying nitrogen which comprises passing purified nitrogen through a getter bed comprising a getter of an alloy of from 15 to 30% by weight of iron and from 85 to 70% by weight of zirconium at a temperature of 20° to 500°C.

14. A superpurifier for purifying an impurity-containing nitrogen gas said superpurifier comprising:

A. an outer shell having a gas inlet through which the inpurity-containing nitrogen gas enters the superpurifier and a gas outlet through which a purified nitrogen gas exits the superpurifier;

B. a gas flow passage within the outer shell extending from the gas inlet to the gas outlet thereby providing fluid communication between the gas inlet and the gas outlet;

C. a getter chamber disposed in the gas flow passage between the gas inlet and the gas outlet;

D. a getter material provided in the getter chamber, said getter material being an alloy of from 15 to 30% by weight iron and 85 to 70% by weight zirconium; and

E. means for heating the getter material and maintaining the getter material at a temperature at which the getter material selectively sorbs impurities from the impurity-containing nitrogen gas without sorbing nitrogen.

15. A superpurifier for purifying an impurity-containing nitrogen gas, said superpurifier comprising:

A. an outer shell having a gas inlet and a gas outlet;

B. a gas flow passage within the outer shell, said gas flow passage extending from the gas gas inlet to the gas outlet thereby providing fluid communication between the gas inlet and the gas outlet;

C. a cartridge detachably mounted in the gas flow passage in the outer shell, said cartridge comprising a perforated metal container packed with a getter material, said getter material comprising an alloy of from 22 to 25% by weight iron and from 75 to 78% by weight zirconium and said getter material being in the form of columnar pellets having a diameter of approximately 3 mm and a height of 4mm; and

D. heating means for maintaining the getter material at a temperature of from 350° to 450°C.

16. A method of purifying an impurity-containing nitrogen gas comprising the steps of:

I. providing a superpurifier comprising:

A. an outer shell having a gas inlet through which the impurity-containing nitrogen gas enters the superpurifier and a gas outlet through which a purified nitrogen gas exits the superpurifier;

B. a gas flow passage within the outer shell extending from the gas inlet to the gas outlet thereby providing fluid communication between the gas inlet and the gas outlet;

C. a getter chamber disposed in the gas flow passage between the gas inlet and the gas outlet;

D. a getter material provided in the getter chamber, said getter material being an alloy of from 15 to 30% by weight iron and 85 to 70% by weight zirconium; and

E. means for heating the getter material and maintaining the getter material at a temperature at which the getter material selectively sorbs impurities from the impurity-containing nitrogen gas without sorbing nitrogen; and

II. heating the getter material to a temperature of 350° to 450°C; and

III. introducing the impurity-containing nitrogen gas into the superpurifier through the gas inlet; and

IV. passing the impurity-containing nitrogen gas through the getter chamber thereby contacting the impurity-containing nitrogen gas with the getter material and sorbing impurities from the impurity-containing nitrogen gas to produce a purified nitrogen gas; and

V. collecting the purified nitrogen gas which exits the superpurifier through the gas outlet.

17. A superpurifier for nitrogen constructed substantially as described herein with reference to, and as illustrated by, any one of Figures 1 to 9, the superpurifier containing a getter as specified in claim 1.

18. A process for purifying nitrogen carried out substantially as described in any one of the Examples herein.

19. Nitrogen whenever purified using apparatus as claimed in any one of claims 1 to 9, 14, 15 and 17.

20. Nitrogen whenever purified by a process or method as claimed in any one of claims 10 to 13, 16 and 18.

21. Any novel feature or any novel combination of features described herein.

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